

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 January 2002 (24.01.2002)

PCT

(10) International Publication Number  
**WO 02/05952 A2**

(51) International Patent Classification<sup>7</sup>: **B01J 29/84,**  
C07C 1/20 [US/US]; c/o UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US).

(21) International Application Number: **PCT/US01/21958**

(74) Common Representative: UOP LLC; 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US).

(22) International Filing Date: 12 July 2001 (12.07.2001)

(25) Filing Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(26) Publication Language: English

(30) Priority Data:  
09/615,816 13 July 2000 (13.07.2000) US

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:

US 09/615,816 (CIP)  
Filed on 13 July 2001 (13.07.2001)

**Published:**

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 02/05952 A2**

(54) Title: ATTRITION RESISTANT CATALYST FOR LIGHT OLEFIN PRODUCTION

(57) Abstract: Catalyst compositions that are effective for the conversion of methanol to light olefins (e.g. ethylene) are disclosed. The catalysts comprise a crystalline metalloaluminophosphate molecular sieve (e.g. SAPO-34) and a matrix material comprising an inorganic oxide binder and a filler, preferably a clay (e.g. kaolin). It has been discovered that by maintaining the content of the molecular sieve at 40 % or less by weight, the overall catalyst attrition resistance is markedly improved.

“ATTRITION RESISTANT CATALYST FOR LIGHT OLEFIN PRODUCTION ”

**BACKGROUND OF THE INVENTION**

The limited supply and increasing cost of crude oil has prompted the search for alternative processes for producing hydrocarbon products. One such process is the conversion of methanol to hydrocarbons and especially light olefins (by light olefins is meant C<sub>2</sub> to C<sub>4</sub> olefins). The interest in the methanol to olefin (MTO) process is based on the fact that methanol can be obtained from coal or natural gas by the production of synthesis gas which is then processed to produce methanol.

Processes for converting methanol to light olefins are well known in the art. Initially aluminosilicates or zeolites were used as the catalysts necessary to carry out the conversion. For example, see US-A-4,238,631 B1, US-A-4,328,384 B1 and US-A-4,423,274 B1. These patents further disclose the deposition of coke onto the zeolites in order to increase selectivity to light olefins and minimize the formation of C<sub>5+</sub> byproducts.

The prior art also discloses that silico aluminophosphates (SAPOs) can be used to catalyze the methanol to olefin process. Thus, US-A-4,499,327 B1 discloses that many of the SAPO family of molecular sieves can be used to convert methanol to olefins. Preferred SAPOs are those that have pores large enough to adsorb xenon (kinetic diameter of 4.0 Å) but small enough to exclude isobutane (kinetic diameter of 5.0 Å). A particularly preferred SAPO is SAPO-34. US-A-4,752,651 B1 discloses the use of nonzeolitic molecular sieves (NZMS) including ELAPOs and MeAPO molecular sieves to catalyze the methanol to olefin reaction.

The effect of the particle size of the molecular sieve on activity has also been documented in US 5,126,308 B1. In the '308 patent it is disclosed that molecular sieves in which 50% of the molecular sieve particles have a particle size less than 1.0 micron and no more than 10% of the particles have a particle size greater than 2.0 microns have increased activity and/or durability. The '308 patent also discloses that restricting the silicon content to 0.005 to 0.05 mole fraction also improves catalytic performance. Further regarding particle size, US-A-5,912,393 discloses that molecular sieves having an average smallest crystal dimension of at least 0.1 microns are favorable in terms of their selectivity toward ethylene versus propylene.

During normal processing conditions for the MTO reaction carbonaceous byproducts, known as coke, deposit and accumulate on the solid catalyst. Eventually, a substantial amount of the catalyst pores become blocked to the extent that a regeneration, or coke burning step, is required to restore the catalyst activity. Catalyst regeneration can  
5 be performed intermittently by temporarily suspending the normal methanol to olefin conversion process and thereafter subjecting the catalyst bed to an oxygen-containing atmosphere at conditions sufficient to combust the catalyst coke. More advantageously, however, the costs associated with downtime can be avoided by transporting at least part of the catalyst to a separate regenerator vessel while maintaining the olefin production  
10 reaction in a reactor vessel that is closely coupled to the regenerator. Movement of the catalyst is accomplished using a fluidized bed in much the same manner as practiced widely in commercial refinery fluidized catalytic cracking (FCC) operations.

It is therefore apparent that the ability of the catalyst to physically withstand the reaction and regeneration environments is a primary consideration relating to the catalyst  
15 used for the conversion of methanol to light olefins. Mechanical strength in this case is most appropriately characterized by the resistance of the catalyst to attrition, or breakage resulting from catalyst-catalyst or catalyst-equipment interactions. These interactions include both direct inter-particle collisions and abrasions caused by catalyst movement past solid surfaces. Catalyst attrition adversely affects the fresh catalyst makeup rate to  
20 the process and hence the average catalyst life. The fines generated from catalyst attrition are normally separated from the reactor and regenerator effluents using cyclone separators, which are effective for capturing particles as small as 10 microns in diameter. The removal of even smaller dust particles is accomplished with electrostatic precipitators and so-called third stage separators. The rate of catalyst attrition therefore  
25 directly affects the sizing requirements and efficiencies of these cyclones and precipitators. Furthermore, incomplete removal of catalyst fines can lead to contamination of the light olefin product stream with solids or possibly the emission of dust particles into the environment.

Attrition resistance is thus a very desirable property of a catalyst used for the conversion of methanol to olefins, and the improvement of catalyst mechanical properties to combat attrition represents an area of ongoing and diligent effort. For example, WO  
30 99/21653 discloses methods of making molecular sieve catalysts for hydrocarbon and

oxygenate conversions, where such methods are designed to increase catalyst attrition resistance. The publication further states that catalysts with the highest amounts of SAPO-34 molecular sieve (e.g. 50 wt-%) incorporated into the formulations gave a better extended attrition index or produced fewer microfines than those having lower amounts of SAPO-34 (e.g. 25 wt-%).

In contrast, applicants have found that catalysts having a reduced amount of crystalline metalloaluminophosphate molecular sieve (e.g. SAPO-34) relative to the amount of matrix material or binder actually show improved attrition resistance.

### SUMMARY OF THE INVENTION

The present invention relates to a catalyst and a process using the catalyst for converting methanol to light olefins. The process comprises contacting the methanol with the catalyst, having improved attrition resistance, at conversion conditions to obtain light olefins. The catalyst comprises a crystalline metalloaluminophosphate molecular sieve having a chemical composition on an anhydrous basis expressed by an empirical formula of  $(EL_xAl_yP_z)O_2$ , where EL is an element selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof; "x" is the mole fraction of EL and has a value of at least 0.005; "y" is the mole fraction of Al and has a value of at least 0.01; and "z" is the mole fraction of P and has a value of at least 0.01; and  $x + y + z = 1$ . The molecular sieve is present in an amount of less than 40% by weight, relative to the catalyst weight. The catalyst further comprises a matrix material comprising an inorganic oxide binder and a filler.

### DETAILED DESCRIPTION OF THE INVENTION

An essential feature of the catalyst of the instant invention is an ELAPO molecular sieve. ELAPOs are molecular sieves that have a three-dimensional microporous framework structure of  $AlO_2$ ,  $PO_2$  and  $ELO_2$  tetrahedral units. Generally the ELAPOs have the empirical formula



where EL is an element selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, "x" is the mole fraction

of EL and has a value of at least 0.005, "y" is the mole fraction of Al and has a value of at least 0.01, "z" is the mole fraction of P and has a value of at least 0.01 and  $x + y + z = 1$ . When EL is a mixture of elements, "x" represents the total amount of the element mixture present. Preferred elements (EL) are silicon, magnesium and cobalt with silicon being especially preferred.

The preparation of various ELAPOs are well known in the art and may be found in US-A-4,554,143 B1 (FeAPO); US-A-4,440,871 B1 (SAPO); US-A-4,853,197 B1 (MAPO, MnAPO, ZnAPO, CoAPO); US-A-4,793,984 B1 (CAPO), US-A-4,752,651 B1 and US-A-4,310,440 B1. Generally, the ELAPO molecular sieves are synthesized by hydrothermal crystallization from a reaction mixture containing reactive sources of EL, aluminum, phosphorus and a templating agent. Reactive sources of EL are the salts of the EL element such as the chloride and nitrate salts. When EL is silicon a preferred source is fumed, colloidal or precipitated silica. Preferred reactive sources of aluminum and phosphorus are pseudo-boehmite alumina and phosphoric acid. Preferred templating agents are amines and quaternary ammonium compounds. An especially preferred templating agent is tetraethylammonium hydroxide (TEAOH).

A preferred method of preparation of an ELAPO molecular sieve having a crystal morphology in which the average smallest crystal dimension is at least 0.1 microns and preferably at least 0.2 microns is described in US-A-5,912,393 B1. As explained in the '393 patent, when crystallites with an average smallest dimension of at least 0.1 microns are used in the catalyst for the conversion of methanol to light olefins, a higher production of ethylene relative to propylene is achieved.

After the initial synthesis, the ELAPOs will usually contain some of the organic templating agent in its pores. In order for the ELAPOs to be active catalysts, the templating agent in the pores must be removed by heating the ELAPO powder in an oxygen-containing atmosphere at a temperature of 200° to 700°C until the template is removed, usually a few hours.

A preferred embodiment of the invention is one in which the element (EL) content of the ELAPO molecular sieve varies from 0.005 to 0.05 mole fraction. If EL is more than one element, then the total concentration of all the elements is between 0.005 and 0.05 mole fraction. An especially preferred embodiment is one in which EL is silicon (usually referred to as SAPO). The SAPOs that can be used in the present invention are

any of those described in US-A-4,440,871 B1; US-A-5,126,308 B1, and US-A-5,191,141 B1. SAPO catalysts that are suitable for the present invention include SAPO-11, SAPO-17, and SAPO-34 with SAPO-34 and SAPO-17 being preferred.

The crystalline metalloaluminophosphate, or ELAPO molecular sieve, is incorporated into solid particles in which the ELAPO is present in an amount effective to promote the desired conversion of methanol to light olefins. In one aspect, the solid particles comprise a catalytically effective amount of the ELAPO molecular sieve and a matrix material comprising an inorganic oxide binder material and also filler to provide a desired level of mechanical strength or attrition resistance of the bound catalyst. It has been determined that the catalyst resistance to attrition is significantly improved when the crystalline metalloaluminophosphate contributes less than 40% of the total catalyst weight and preferably less than 20%. Thus, the total matrix material is present in an amount of at least 60% by weight, and preferably at least 80% by weight, relative to the total catalyst weight. In a preferred embodiment, this amount of matrix material will provide a bound catalyst having a weight loss of less than 1% of the catalyst weight per hour, as measured according to a standard attrition test designed for fluidized bed catalysts. Preferably, in order to ensure that the ELAPO molecular sieve is present in a catalytically effective amount, the matrix material comprises less than 95% by weight of the catalyst composition. In some cases, however, it may be feasible to use a catalyst comprising even more than 95% by weight of the matrix material, depending on the particular reaction chemistry and physical limitations imposed by the reactor size.

In addition to enhancing the catalyst strength properties, the matrix material allows the molecular sieve crystallite powder to be bound into larger particle sizes suitable for commercial catalytic processes. The ELAPO/matrix material mixture may be formed into a wide variety of shapes including extrudates, spheres, pills, and the like. The matrix material is often, to some extent, porous in nature and may or may not be effective to promote the desired conversion of methanol to light olefins. The matrix material may also promote conversion of the feed stream and often provides reduced selectivity to the desired product or products relative to the catalyst.

The matrix material comprises an inorganic oxide binder and a filler. Examples of preferred binder materials include, but are not limited to, alumina, silica, aluminum phosphate, silica-alumina, zirconia, titania, and mixtures thereof. Filler materials can

include, for example, synthetic and naturally occurring substances such as clays, metal oxides, silicas, aluminas, silica-aluminas, and mixtures thereof. In referring to the types of binders and fillers that may be used, it should be noted that the term silica-alumina does not mean a physical mixture of silica and alumina but means an acidic and amorphous material that has been cogelled or coprecipitated. This term is well known in the art and is described, for example, in US-A-3,909,450 B1; US-A-3,274,124 B1 and US-A-4,988,659 B1. In this respect, it is possible to form other cogelled or coprecipitated amorphous materials that will also be effective as either binder or filler materials. These include silica-magnesias, silica-zirconias, silica-thorias, silica-berylbias, silica-titanias, silica-alumina-thorias, silica-alumina-zirconias, aluminophosphates, mixtures of these, and the like. Preferably, the filler is a clay, since clays are known to be essentially inert under a wide range of reaction conditions. Suitable clays include commercially available products such as kaolin, kaolinite, montmorillonite, saponite, and bentonite. These clays can be used as mined in their natural state, or they may also be employed in highly active forms, typically activated by an acid treatment procedure. Commercial suppliers of these clays include Thiele Kaolin Company (Sandersville, GA), American Colloidal Co. (Arlington Heights, IL), GSA Resources, Inc. (Tucson, AZ), Albion Kaolin Co. (Hephzibah, GA), and others.

In preparing the catalyst of the present invention, a slurry of the ELAPO crystalline metalloaluminophosphate powder, the filler, and the inorganic oxide binder is formed. As mentioned, the slurry will contain an appropriate sol, or carrier material, of the inorganic oxide binder used for suspending the molecular sieve. In the case of incorporating alumina, silica, magnesia, zirconia, or titania binders into the bound catalyst composition of the present invention; it is appropriate to use a hydrosol. For example, any of the transitional aluminas can be mixed with water and an acid to give an aluminum sol. Acids for this application may include inorganic acids such as nitric, hydrochloric, and sulfuric, or organic acids, especially carboxylic acids such as formic, acetic, propionic, and the like. Alternatively, an aluminum sol can be made by for example, dissolving aluminum metal in hydrochloric acid and then mixing the aluminum sol with the alumina powder. When an alumina binder is desired, it is also possible to use a solution of boehmite or aluminum nitrate in place of the aluminum sol.



Types of silica sols used to form a bound catalyst for use in the MTO process are commercially available as aquasols or organosols containing dispersed colloidal silica particles. For example, sodium silicate can be used as a silica sol and combined with an acidic aluminum sol to ultimately yield a silica-alumina binder in the final catalyst.

5      Otherwise, a silica gel may also be used to provide a silica binder in the molecular sieve catalyst. Silicic acid is another possible source of silica. If a magnesia binder is desired, the starting slurry will contain hydrolyzed magnesium alkoxide. When a zirconia binder is used for the catalyst preparation, the preferred starting acidic sol is an aqueous zirconium acetate solution, which is preferably combined with a urea gelling agent.

10     When a titania binder is used, the acidic sol is preferably a solution of titanyl oxychloride, which is also preferably combined with a urea gelling agent. Acidic colloidal suspensions of various inorganic oxides are also available from commercial suppliers such as Nano Technologies, Inc. (Ashland, MA). The amount of sol added to the slurry is based on a typical binder contribution from 5% to 50% of the weight of the

15     bound molecular sieve catalyst. Preferably, the binder is present in an amount from 10% to 30% by weight. As mentioned, the entire contribution of the matrix material (i.e. both the inorganic oxide binder and filler) in the final catalyst is at least 60%, in order to limit the amount of crystalline aluminophosphate molecular sieve to less than 40% by weight. Preferably, the total matrix material accounts for at least 80% by weight, and more

20     preferably from 80% to 95% by weight of the catalyst. Those skilled in the art will readily appreciate the relationship between the molecular sieve:sol weight ratio of the slurry and the resulting molecular sieve:binder ratio in the catalyst.

As discussed, it is also required that the slurry contain a filler in addition to the sol of the inorganic oxide binder. The filler may itself be an inorganic oxide (e.g. alumina) that is incorporated into the slurry in a powdered form rather than a sol.

25     Preferably, the filler is a clay selected from the group of suitable clays provided previously. It has been determined that the clay improves the overall strength of the bound catalyst, and this improvement can be measured by the amount of finished catalyst material lost during a standard attrition test (i.e. attrition loss). Loss of the catalyst by attrition is measured by fluidizing the catalyst in air for a given period of time, collecting and weighing the fines generated, and then calculating an attrition loss as an average percent of the initial catalyst weight per hour. It has been found that by using an amount

of molecular sieve of less than 40%, and preferably less than 20% relative to the total catalyst weight, the attrition loss can be controlled to less than 1%, preferably less than 0.8%, and more preferably less than 0.5% by weight per hour.

5 It is also within the scope of the present invention to include other components in the slurry that may have an impact on the final catalyst properties. For example, WO 99/21653 discloses the use of an external phosphorous source, including potential sources of phosphorous and relative amounts desired in the catalyst composition.

10 Depending on the average particle size of agglomerated molecular sieve crystallites present in the slurry, it may be desired to mill the slurry in order to break these agglomerates apart, thereby reducing the agglomerate particle size and/or giving a narrower particle size distribution. Milling can be done by means known in the art such as ball milling for times from 30 minutes to 5 hours and preferably from 1.5 to 3 hours. It is believed that using a slurry with a particle size distribution that has been adjusted in this manner improves the structural characteristics of the bound molecular sieve catalyst.  
15 Care must be taken not to mill the slurry so extensively as to destroy the crystallite structure of the molecular sieve.

It should also be noted that, in addition to the molecular sieve powder, sol of the inorganic oxide binder, and filler, the slurry will often contain water. The amount of water is often adjusted after any milling operation in order to obtain a viscosity of the  
20 milled slurry in the range from 30 to 600 centipoise. Prior to drying, it is generally preferred that the slurry components are well mixed to ensure a uniform slurry composition. A period of high shear mixing of 15 minutes, for example, is effective in most cases for obtaining the proper uniformity. It is important to initiate the subsequent drying step prior to the onset of gelling of the slurry, usually 1 hour after mixing.

25 The well-mixed slurry, either with or without prior milling, is then dried at a temperature from 50°C to 300°C for a time from 1 to 24 hours to form dried, shaped particles. These particles may or may not be subsequently milled or otherwise reduced in size at this point to provide catalyst physical properties that in turn lead to the ultimately desired pressure drop characteristics, fluidization velocity, diffusion resistance, and other  
30 properties. The dried, shaped particles have an average effective diameter broadly from 10 to 300 microns, and preferably from 20 to 150 microns. By effective diameter is meant, for non-spherical shapes, the diameter that the shaped particle would have if it

were molded into a sphere. In a preferred embodiment, the dried, shaped particles are substantially spherical in shape. In this case the resulting catalyst form is often referred to as microspheres.

A preferred method for drying the slurry is known in the art as spray drying.  
5 Using this technique, the slurry is fed into a nozzle that breaks the slurry into small droplets. The particles are thereafter dried in a co-current or counter-current flow of air through the spray drier. Those skilled in the art will recognize that the size of the dried, shaped particles exiting the spray drier is determined by a number of factors including diameter and height of the apparatus, nozzle type, and wheel RPM if a disk atomizer is  
10 used. Undersized particles exiting the spray drier can be separated and returned to the entering slurry, thereby improving the overall catalyst yield. Often, however, it is desired to grind this recycle stream of particles to less than 5 microns before mixing them with the slurry feeding the spray drier. An advantage of using the spray drying technique is the ability, if desired, to produce dried, shaped particles that are substantially spherical and  
15 thus suitable for dynamic, moving bed catalytic processes. Regardless of the method of drying, however, it is preferred that the particles have an effective diameter from 10 to 300 microns.

The dried, shaped catalyst particles may optionally be finished by contacting them with an aqueous exchange solution of an ionic compound. The aqueous exchange  
20 solution is characterized in that it is effective for removing undesired metallic cations that may occupy the ion exchange sites of the molecular sieve. For example, the crystalline aluminophosphate exchange sites are often occupied to some extent by sodium, potassium, magnesium, or other cations. These species can originate from inorganic template material present in the molecular sieve or, more commonly, stem  
25 from the inorganic oxide binder source material (e.g. aluminum sol). In the processing service for which the catalyst is designed (e.g. the conversion of methanol to olefins) these metal cations can promote side reactions, slow the desired reaction rate, or otherwise complicate the catalysis of the desired reaction. Some sources of the inorganic oxide binder (e.g. silicic acid) are essentially free of undesired metal cations and  
30 therefore the dried particles produced using such sources would not necessarily require contact with an exchange solution. Water washing both before and after the finishing step may be desired to flush the catalyst of undesired solids and/or residual exchange solution.

Preferably, the exchange solution comprises an ammonium compound, and in particular ammonium sulfate, ammonium carbonate, ammonium bicarbonate, ammonium nitrate, ammonium hydroxide, and various ammonium halides have been found effective for the finishing step. This effectiveness is based on the ability of the exchange solution to remove the metallic cation contaminants mentioned above and thereby convert the crystalline aluminophosphate molecular sieve component of the catalyst to substantially its hydrogen form. Thus, the finishing step converts metallic cation-exchanged sites of the molecular sieve to desired hydrogen-exchanged sites. Conditions for the finishing step include an exchange solution temperature from 5°C to 95°C and a contacting time from 0.5 to 10 hours, depending on the temperature and other factors. Finishing may be performed either batch wise or continuously.

Finally, the dried, shaped particles, with or without finishing, are calcined at a temperature from 400°C to 900°C in an air environment for a time from 1 to 10 hours to effectively set the inorganic oxide binder. The calcination step also removes any remaining template material that may be present within the crystalline metalloaluminophosphate molecular sieve. In some cases, the catalyst may be activated in a modified calcination step wherein the organic template is first decomposed in a flow of pure nitrogen. The oxygen concentration is then gradually increased to combust any residual hydrocarbons in the molecular sieve. It is also possible to combine the drying and calcining operations into a single step.

The conversion of methanol to light olefins is effected by contacting the methanol with the ELAPO molecular sieve-containing catalyst at conversion conditions, thereby forming the desired light olefins. The methanol can be in the liquid or vapor phase with the vapor phase being preferred. Contacting the methanol with the ELAPO catalyst can be done in a continuous mode or a batch mode with a continuous mode being preferred. The amount of time that the methanol is in contact with the ELAPO catalyst must be sufficient to convert the methanol to the desired light olefin products. When the process is carried out in a batch process, the contact time varies from 0.001 hr. to 1 hr. and preferably from 0.01 hr. to 1.0 hr. The longer contact times are used at lower temperatures while shorter times are used at higher temperatures. Further, when the process is carried out in a continuous mode, the weight hourly space velocity (WHSV) based on methanol can vary from 1 hr<sup>-1</sup> to 1000 hr<sup>-1</sup> and preferably from 1 hr<sup>-1</sup> to 100

hr<sup>-1</sup>. As is understood in the art, the weight hourly space velocity is the weight flow of the methanol divided by the catalyst weight. This term provides a measure of how many equivalent weights of the catalyst inventory are processed every hour as methanol.

Generally, the process must be carried out at elevated temperatures in order to form light olefins at a fast enough rate. Thus, the process is carried out at a temperature of 300°C to 600°C, preferably from 400°C to 550°C and most preferably from 450°C to 525°C. The process may be carried out over a wide range of pressure including autogenous pressure. Thus, the pressure can vary from 0 kPa (0 psig) to 1724 kPa (250 psig) and preferably from 34 kPa (5 psig) to 345 kPa (50 psig).

Optionally, the methanol feedstock may be diluted with an inert diluent in order to more efficiently convert the methanol to olefins. Examples of the diluents which may be used are helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, steam, paraffinic hydrocarbons, e.g., methane, aromatic hydrocarbons, e.g., benzene, toluene and mixtures thereof. The amount of diluent used can vary considerably and is usually from 5 to 90 mole percent of the feedstock and preferably from 25 to 75 mole percent.

The actual configuration of the reaction zone may be any well-known catalyst reaction apparatus known in the art. Thus, a single reaction zone or a number of zones arranged in series or parallel may be used. In such reaction zones the methanol feedstock is passed through a bed containing the ELAPO catalyst. When multiple reaction zones are used, one or more ELAPO catalysts may be used in series to produce the desired product mixture. Instead of a fixed bed, a dynamic bed system, e.g., fluidized or moving, may be used. Such a dynamic system would facilitate any regeneration of the ELAPO catalyst that may be required. If regeneration is required, the ELAPO catalyst can be continuously introduced as a moving bed to a regeneration zone where it can be regenerated by means such as oxidation in an oxygen-containing atmosphere to remove carbonaceous materials.

As stated previously, the attrition resistant catalyst of the present invention is particularly suited to the rigorous environment of a dynamic, fluidized bed process. This mode of operation allows continuous regeneration of all or part of the catalyst inventory after its use in the conversion process. The ability to regenerate the catalyst in this manner is particularly valuable in cases such as the MTO process, where, without regeneration, rapid coking would quickly expend the catalyst activity, thereby requiring

the process unit to be shut down for off-line regeneration or reloading of the catalyst. These procedures are normally associated with considerable lost operating time and revenue.

5 The following examples are presented in illustration of this invention and are not intended as undue limitations on the generally broad scope of the invention as set forth in the appended claims.

#### EXAMPLES 1-6

To investigate the effect of the crystalline aluminophosphate molecular sieve catalyst composition on attrition, six catalyst samples were prepared according to the preparation procedure outlined previously. The slurry in this example contained the molecular sieve SAPO-34, kaolin clay, and the sols of both silica and alumina. Specifically, the silica-alumina binder system comprised a 2:1 volume ratio mixture of acidified aluminum sulfate (commonly called acid alum) and sodium silicate. The alum contained approximately 12.8 wt-% free H<sub>2</sub>SO<sub>4</sub> and 2.5 wt-% Al<sub>2</sub>O<sub>3</sub> and the sodium silicate solution was 16% SiO<sub>2</sub> and had a ratio of Na<sub>2</sub>O:SiO<sub>2</sub> of 3.2.

10 The solution containing the sources of alumina and silica used in the binder was mixed in an eductor under controlled conditions of temperature and pH. After mixing, the binder system was added to a vessel that was constantly stirred using a high shear mixer. Kaolin clay (R-87, commercially available from Thiele Kaolin Company) was 15 then slowly introduced. To complete the slurry preparation, milled SAPO-34 molecular sieve was added to the mixture.

20 After 10-15 minutes of stirring, the slurry was pumped to a spray dryer and dried to form spherical shaped particles (i.e. microspheres) having an average diameter of 70-100 microns. Conditions used for the spray drying procedure included inlet and outlet 25 temperatures of 340°C and 135°C, respectively. The particles were then ion-exchanged with an ammonium sulfate solution to obtain substantially the hydrogen form of the molecular sieve. After this finishing step, the particles were dried and calcined, according to procedures described earlier, to yield the final catalyst.

30 The six catalyst samples represented two distinct compositions, with three samples of each. The first composition was 40% SAPO-34, 40% kaolin clay, and 20% inorganic oxide binder by weight. The inorganic oxide binder, as explained above, was a

mixture of silica/alumina in a ratio of 90/10 by weight. The second composition was 20% SAPO-34, 60% kaolin clay, and 20% inorganic oxide binder by weight. Again, the inorganic oxide binder was an approximately 90/10 weight ratio mixture of silica and alumina.

5       The attrition resistance of the various catalyst samples was measured after calcination at 650°C. To measure attrition resistance, a standardized test for fluidized bed catalysts was used. The procedure involved placing a sample of each catalyst in a tube through which humidified air was passed at a predetermined flow rate to provide a fluidized environment. Catalyst fines were collected, separated from the catalyst, and weighed hourly to determine the rate of catalyst breakage. An attrition loss, expressed in terms of an average weight percent breakage per hour, relative to the initially loaded catalyst weight, was calculated. The test was stopped after 5 hours.  
10

A summary of the various catalyst compositions, finishing (i.e. exchange) conditions, and attrition results is provided in Table 1.

15

TABLE I

## ATTRITION RESISTANCE OF VARIOUS MOLECULAR SIEVE CATALYSTS

EXAMPLE	CATALYST COMPOSITION, wt-%			FINISHING CONDITIONS		ATTRITION (wt-% / hr)
	SAPO-34	Kaolin Clay	Inorganic Oxide Binder	Solution	Temp.	
1	40%	40%	20%	$(NH_4)_2SO_4$	7.2°C	0.9
2	20%	60%	20%	$(NH_4)_2SO_4$	7.2°C	0.2
3	40%	40%	20%	$(NH_4)_2SO_4$	35°C	0.7
4	40%	40%	20%	$(NH_4)_2CO_3$	7.2°C	0.7
5	20%	60%	20%	$(NH_4)_2CO_3$	7.2°C	0.2
6	40%	40%	20%	$(NH_4)_2CO_3$	35°C	0.7

20     Since commercial MTO reactor designs are typically not significantly restricted with regard to the total catalyst loading that may be used, the 20% by weight SAPO-34 composition can readily replace existing catalysts having a higher content molecular sieve content. Therefore, a reduction in the SAPO-34 content of spray-dried catalysts to less than 40% is a practical way to reduce catalyst losses due to fines formation. Catalysts having a SAPO-34 content preferably of less than 20% and even in some cases as low as

5% or less, with the remainder being the matrix material (i.e. clay or inorganic oxide binder), provide a superior alternative to current formulations.

CLAIMS:

1. A catalyst for converting methanol to light olefins comprising a crystalline metalloaluminophosphate molecular sieve and a matrix material, the catalyst characterized in that the crystalline metalloaluminophosphate has an empirical chemical composition on an anhydrous basis expressed by the formula:



where EL is an element selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof; "x" is the mole fraction of EL and has a value of at least 0.005; "y" is the mole fraction of Al and has a value of at least 0.01; "z" is the mole fraction of P and has a value of at least 0.01; and  $x + y + z = 1$ , the matrix material comprises an inorganic oxide binder and a filler, and the molecular sieve is present in an amount of less than 40% by weight, relative to the catalyst weight.

10 2. The catalyst of claim 1 where the EL element is selected from the group consisting of silicon, magnesium, cobalt, nickel, and mixtures thereof.

15 3. The catalyst of claims 1 or 2 where the EL element is silicon.

4. The catalyst of any of claims 1 to 3 where the binder is selected from the group consisting of alumina, silica, aluminum phosphate, silica-alumina, zirconia, titania, and mixtures thereof.

20 5. The catalyst of any of claims 1 to 4 where the filler is a clay selected from the group consisting of kaolin, kaolinite, montmorillonite, saponite, bentonite, and mixtures thereof.

6. The catalyst of any of claims 1 to 5 where the molecular sieve is present in an amount from 5% to 20% by weight, relative to the catalyst weight.

25 7. The catalyst of any of claims 1 to 6 where the inorganic oxide binder is present in an amount from 10% to 30% by weight, relative to the catalyst weight.

8. The catalyst of any of claims 1 to 7 where the catalyst attrition loss is less than 1% by weight per hour.

30 9. The use of catalyst of any claims 1 to 8 in a process for converting methanol to light olefins the process comprising contacting the catalyst with methanol at conversion conditions to provide olefins.

10. The process of claim 9 where the conversion conditions are a temperature from 300°C to 600°C, a pressure from 0 kPa to 17224 kPa (250 psig) and a weight hourly space velocity from 1 to 100 hr<sup>-1</sup>.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
24 January 2002 (24.01.2002)

PCT

(10) International Publication Number  
**WO 02/05952 A3**

(51) International Patent Classification<sup>7</sup>: **B01J 29/84,**  
C07C 1/20 [US/US]; c/o UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US).

(21) International Application Number: PCT/US01/21958 (74) Common Representative: UOP LLC: 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US).

(22) International Filing Date: 12 July 2001 (12.07.2001) (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/615,816 13 July 2000 (13.07.2000) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:  
US 09/615,816 (CIP)  
Filed on 13 July 2001 (13.07.2001) (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **UOP LLC** [US/US]; 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US).  
Published:  
— with international search report

(72) Inventors; and  
(75) Inventors/Applicants (*for US only*): **BARGER, Paul, T.** [US/US]; c/o UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US). **MARKER, Terry, L.** [US/US]; c/o UOP LLC, 25 East Algonquin Road, Des Plaines, IL 60017-5017 (US). **KARCH, John, A.**



**WO 02/05952 A3**

(54) Title: ATTRITION RESISTANT CATALYST FOR LIGHT OLEFIN PRODUCTION

(57) Abstract: Catalyst compositions that are effective for the conversion of methanol to light olefins (e.g. ethylene) are disclosed. The catalysts comprise a crystalline metalloaluminophosphate molecular sieve (e.g. SAPO-34) and a matrix material comprising an inorganic oxide binder and a filler, preferably a clay (e.g. kaolin). It has been discovered that by maintaining the content of the molecular sieve at 40 % or less by weight, the overall catalyst attrition resistance is markedly improved.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/21958

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 B01J29/84 C07C1/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 B01J C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 21651 A (EXXON CHEMICAL PATENTS INC) 6 May 1999 (1999-05-06) the whole document ----	1-5,7-10
X	US 5 914 433 A (MARKER TERRY L) 22 June 1999 (1999-06-22) column 6, line 55 -column 7, line 67 example I ----	1-5,7-10
X	EP 0 209 793 A (GRACE W R & CO) 28 January 1987 (1987-01-28) page 7, line 18 -page 8, line 7 examples 3,4 ----	1-8
X	EP 0 496 226 A (GRACE W R & CO) 29 July 1992 (1992-07-29) page 2, line 44 - line 56 page 3, line 21 - line 22 -----	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

11 January 2002

Date of mailing of the international search report

21/01/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
 Fax (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 01/21958

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9921651	A	06-05-1999	AU WO	9805598 A 9921651 A1		17-05-1999 06-05-1999
US 5914433	A	22-06-1999	NONE			
EP 0209793	A	28-01-1987	US AT AU BR CA DE EP ES JP NO US	4681864 A 41882 T 5983386 A 8603316 A 1269087 A1 3662647 D1 0209793 A1 2000921 A6 62038243 A 862842 A ,B, 4764269 A		21-07-1987 15-04-1989 22-01-1987 24-02-1987 15-05-1990 11-05-1989 28-01-1987 01-04-1988 19-02-1987 16-01-1987 16-08-1988
EP 0496226	A	29-07-1992	US BR CA DE DE EP ES JP MX US	5194412 A 9200112 A 2057738 A1 69201648 D1 69201648 T2 0496226 A1 2070530 T3 4354541 A 9200260 A1 5286369 A		16-03-1993 06-10-1992 23-07-1992 20-04-1995 13-07-1995 29-07-1992 01-06-1995 08-12-1992 01-07-1992 15-02-1994